Electronic supplementary information

Shape-controlled synthesis of CO-free Pd nanocrystals with the use of formic acid as reducing agent

Shixiong Bao,[ab] Xuan Yang,[a] Ming Luo,[a] Shan Zhou,[c] Xue Wang,[ab] Zhaoxiong Xie,[b] and Younan Xia*[ac]

[a] The Wallace H. Coulter Department of Biomedical Engineering, Georgia Institute of Technology and Emory University, Atlanta, Georgia 30332, United States

[b] State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, and Department of Chemistry, Xiamen University, Xiamen, Fujian 361005, P. R. China

[c] School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

*Correspondence to: younan.xia@bme.gatech.edu

Chemicals. Sodium tetrachloropalladate(II) (Na_2PdCl_4), poly(vinyl pyrrolidone) of 55000 in molecular weight (PVP-55), formic acid (FA), L-ascorbic acid (AA), formaldehyde (HCHO) and potassium bromide (KBr) were all purchased from Sigma-Aldrich. All the chemicals were used as received. Deionized (DI) water with a resistivity of 18.2 MΩ cm was used throughout experiments.

Synthesis of Pd nanocrystals. In a typical synthesis of Pd nanocubes with different sizes, 8.0 mL of an aqueous solution containing PVP-55 (105 mg, 118 mM, with the concentration calculated in terms of the repeating unit of PVP with a molar mass of 111 g/mol), FA (15 μL, 39 mM), and different amounts of KBr were mixed in a 20 mL vial, which was sealed and heated under magnetic stirring at 80 °C for 10 min. Next, 3.0 mL of an aqueous solution containing Na_2PdCl_4 (57 mg, 64 mM) was added rapidly using a pipette. Once the vial was re-capped, the synthesis was allowed to proceed at 80 °C for 3 h. The solid products were collected by centrifugation at 55000 rpm for 30 min and washed three times with water to remove excess PVP. Finally, the nanocubes were re-dispersed in 11 mL of water for storage and used as seeds for growth. For the preparation of samples shown in Figure 1, the procedure was essentially the same, except for the absence of KBr and the involvement of different reducing agents. For ATR-FT-IR measurements, the nanoparticles were washed with water two more times and re-dispersed in ethanol.

Seed-mediated growth of Pd nanocrystals with different shapes. In a typical process, 8.0 mL of an aqueous suspension of the as-prepared Pd seeds (0.3 mL), PVP-55 (105 mg, 118 mM in final concentration), and FA (15 μL, 39 mM in final concentration) was placed in a 20 mL vial and heated at 60 °C in an oil bath under magnetic stirring. After 10 min, 3.0 mL of an aqueous solution containing different amounts of Na_2PdCl_4 was added in one shot using a pipette to initiate growth. The synthesis was allowed to proceed at 60 °C for 3 h. The solid products were collected by centrifugation at 13000 rpm for 15 min and washed with water three times. For ATR-FT-IR measurements, the nanoparticles were washed with water two more times and then re-dispersed in ethanol.

Characterizations. TEM images were taken using a Hitachi HT7700 microscope operated at 120 kV. The sample for TEM analysis was prepared by drying a drop of the nanocrystal suspension on a carbon-coated copper grid under ambient conditions. ATR-FT-IR spectroscopy measurements were performed using a Varian 640 Fourier transform infrared spectrometer equipped with an internal reflection element made of diamond (45° for the angle of incidence, and three active reflections). Before the measurements, the crystal surface was washed using ethanol to remove any contaminant. The sample for analysis (about 10 μL of the suspension of nanoparticles in ethanol) was drop-cast on top of the crystal and dried under ambient conditions. IR spectra were recorded in the range of 4000–400 cm^{-1} with a resolution of 1 cm^{-1} using a cooled deuterated and L-alanine-doped triglycine sulfate (DLaTGS) detector.

Table S1. Statistics of various morphologies in the sample shown in **Fig. 1a**, which was prepared in an aqueous solution with formic acid as a reducing agent in the absence of KBr.

Morphology	**Frequency (%)**
Truncated octahedra	74.9
Triangular plates	14.2
Icosahedra	2.4
Decahedra	3.7
Others	4.8

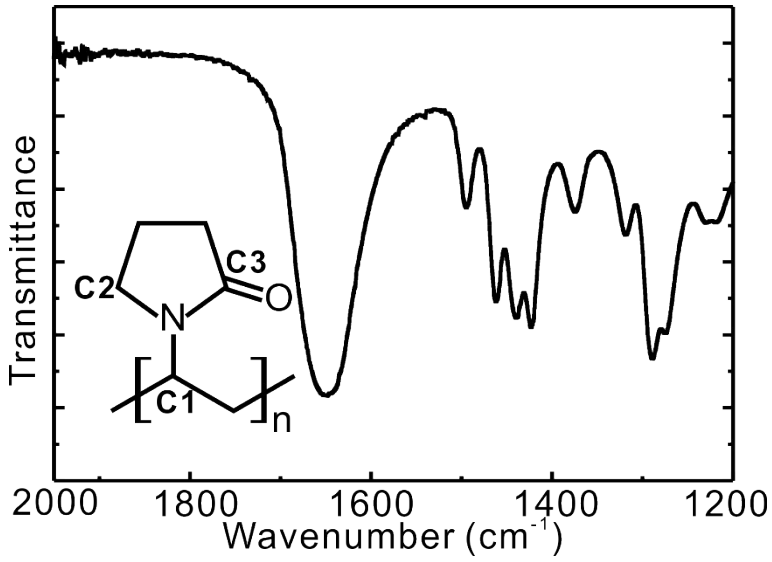

Fig. S1 ATR-FT-IR spectrum of poly(vinyl pyrrolidone) (PVP).

Table S2. The IR bands of PVP shown in **Fig. S1** and their corresponding assignments.

Vibrational mode	IR band
N−C stretch of N−CH_2 (N−C1)	1277
N−C stretch of N−CH_2 (N−C2)	1292
C−H_2 wag	1321
C−H bend	1384
C−H_2 scissor	1424
C−H_2 scissor	1442
C−H_2 scissor	1464
N−C stretch of N−C=O (N−C3)	1499
C=O stretch	1659

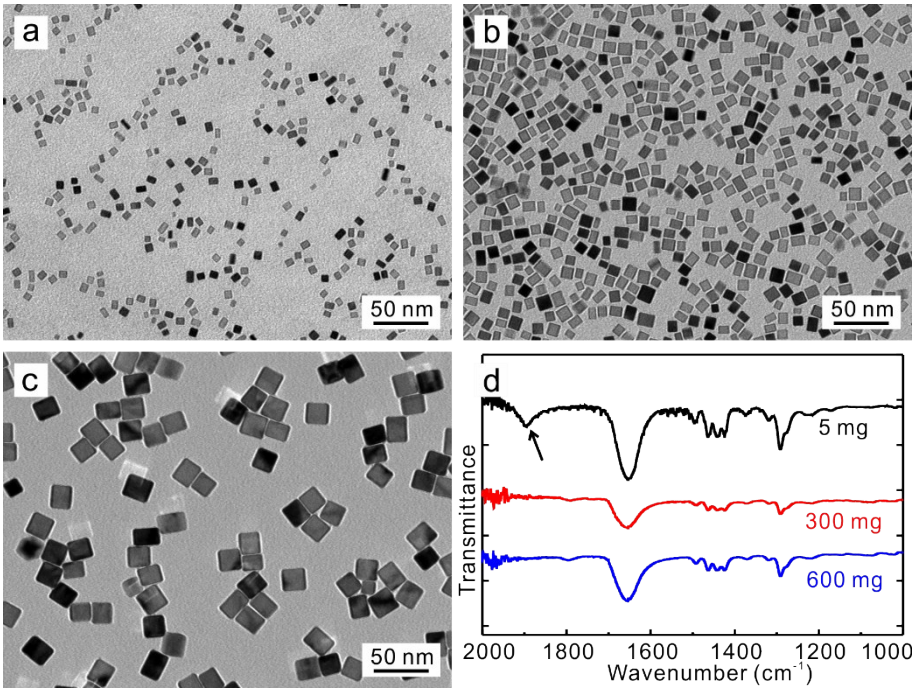

Fig. S2 (a-c) TEM images of the Pd nanocubes prepared in aqueous solutions containing 60 mg of ascorbic acid and different amounts of KBr: (a) 5 mg, (b) 300 mg, (c) 600 mg. (d) ATR-FT-IR spectra recorded from the Pd nanocrystals synthesized using different amounts of KBr (the spectra were offset for clarity).

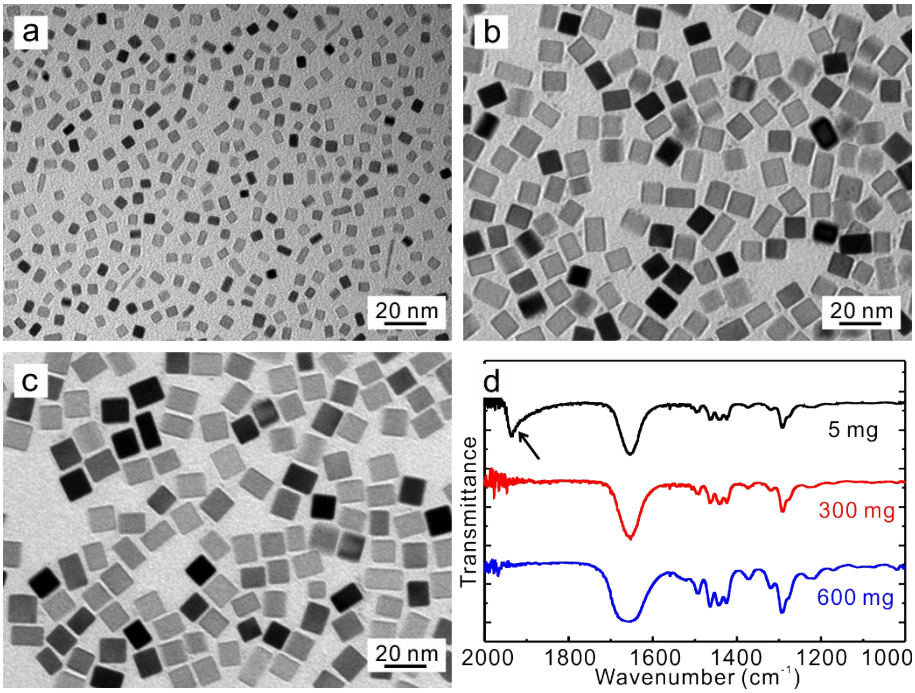

Fig. S3 (a-c) TEM images of the Pd nanocubes prepared in aqueous solutions containing 30 μL of formaldehyde and different amounts of KBr: (a) 5 mg, (b) 300 mg, (c) 600 mg. (d) ATR-FT-IR spectra recorded from the Pd nanocrystals synthesized using different amounts of KBr (the spectra were offset for clarity).

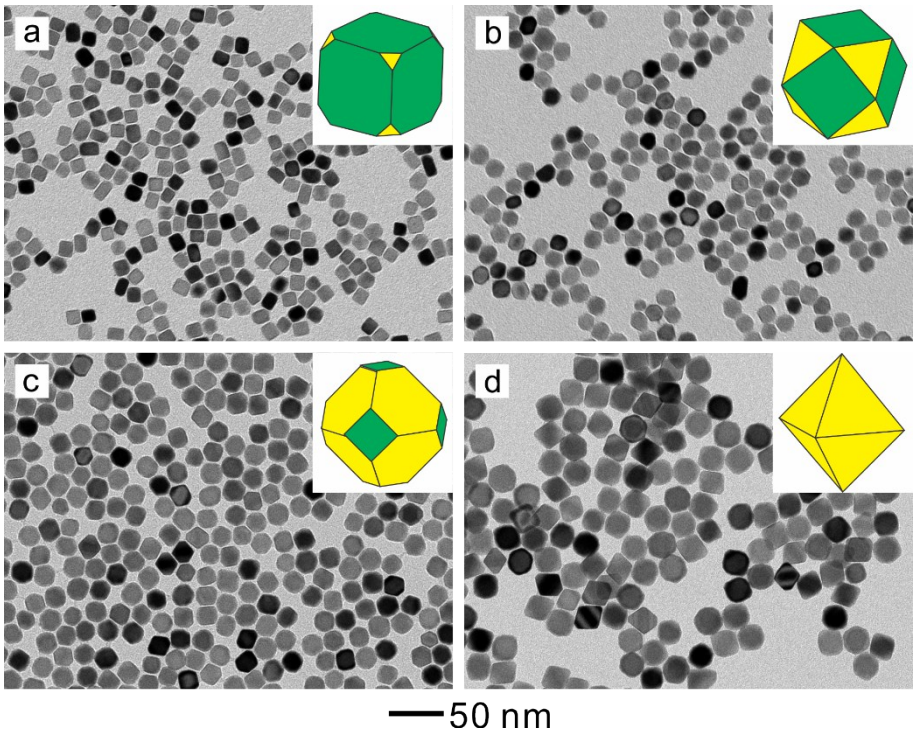

Fig. S4 (a-d) TEM images of the Pd polyhedra prepared by varying the amount of Pd cubic seeds while fixing the amount of Na_2PdCl_4 precursor: (a) 0.9 mL, (b) 0.6 mL, (c) 0.45 mL, and (d) 0.15 mL. The insets show geometrical models of individual nanocrystals. The {111} and {100} facets are shown in yellow and green colors, respectively.

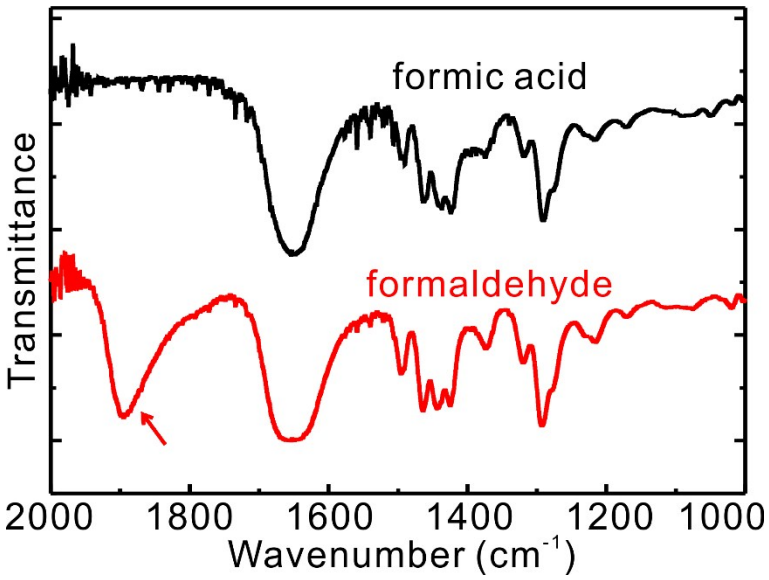

Fig. S5 ATR-FT-IR spectra of the Pd octahedra synthesized using formic acid (black) and formaldehyde (red) as reducing agents, respectively (the spectra were offset for clarity).

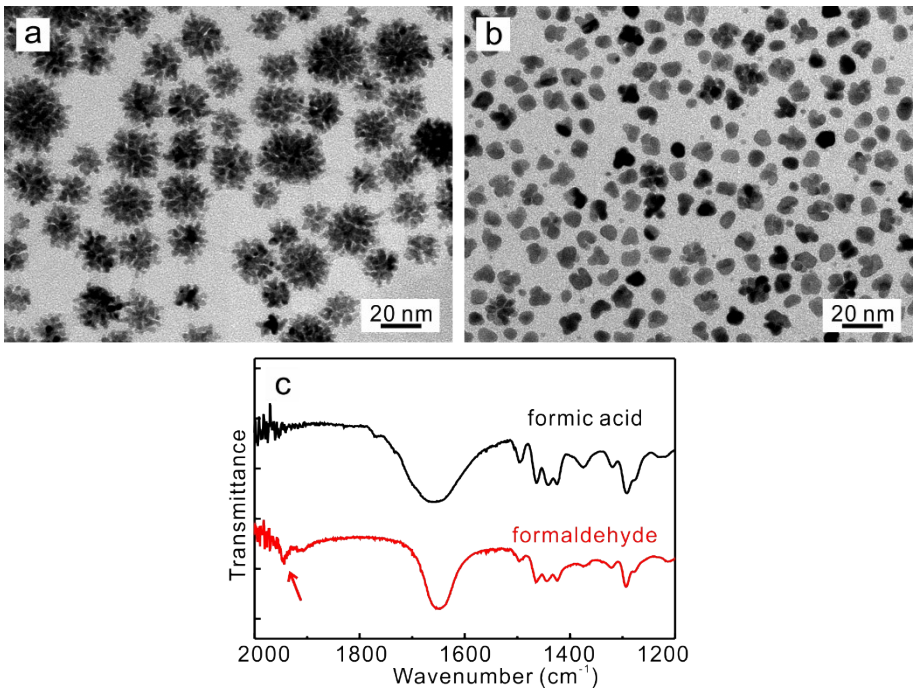

Fig. S6 (a, b) TEM images of Pt nanocrystals prepared in aqueous solutions containing (a) 15 μL of formic acid and (b) 30 μL of formaldehyde, respectively. (c) ATR-FT-IR spectra recorded from the Pt nanocrystals synthesized using different reducing agents (the spectra were offset for clarity).